REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave Blank*)

2. REPORT DATE

See Title Page

3. REPORT TYPE AND DATES COVERED

1 February 1987 to 31 January 1991

4. TITLE AND SUBTITLE

Use Title on Reprint

5. FUNDING NUMBERS

N00014-87-C-0146
0R0A444C-
43051
43051S4

6. AUTHOR(S)

See Individual Articles

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Vanderbilt University
Nashville TN 37332
(615-322-2786)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Each Paper Summarized on first page. Journal articles submitted as contract reports. All work performed under Government contract.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

See first page of Article

19960104 064

14. SUBJECT TERMS

Free Electron Lasers Medicine Biology
Biomedical Instrumentation
Energy Cells

15. NUMBER OF PAGES

00

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18
298-102

D.G. Harris and P.M. Shay, Eds., LASERS '89:1020 (McLean, VA: S.T.S. Press, 1990) Proceedings

II-C.

DEFECT FORMATION IN FUSED SILICAS DUE TO PHOTON IRRADIATION AT 5 AND 50 EV

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Abstract

We have compared the paramagnetic defect formation in two types of pure fused silica glass irradiated with intense photon fluxes at 5 eV (KrF laser) and 50 eV (undulator beam from Aladdin Synchrotron Light Source), using electron paramagnetic resonance spectroscopy with a frequency of 9.7 GHz and sample temperatures of 110 and 300K. The 5 eV photons produce approximately 10^{-14} paramagnetic defects per photon and the 50 eV photons produce approximately 10^{-5} defects per photon. The ratio of E' centers to oxygen related centers is ~10 times greater for 5 eV photons than for 50 eV photons in type III silica.

Introduction

Intrinsic defects in silicas have drawn considerable attention since Weeks initially identified and characterized the E' center in 1956.[1] This attention results from increased understanding of the scientific and technological importance of defects in a wide variety of materials. Many questions about defects in SiO_2 have not been resolved. Defects affect several important applications of silicas. These include optical fibers, both core and cladding regions, and VLSI's (Very Large Scale Integrated Circuits) in which SiO_2 functions as an insulator or passivating layer.

Many interesting phenomena have been discovered with improvements of brightness, pulse duration and the wavelength-tunability of light sources. Stathis and Kastner[2] reported that different defects are created in silicas by 5.0, 6.4, and 7.9 eV photons from excimer lasers whose energies are all smaller than the bandgap energy of silica, which is almost 10 eV.[3,4] They found that 5.0 eV photons are the most efficient in producing E' centers.[3] They also observed that 7.9 eV photons introduced different defects in dry and wet silicas.

The purpose of this work was to determine the relative and absolute efficiency of 5 and 50 eV photons in producing intrinsic defects in silicas. Five eV photons were produced by a KrF excimer laser and the 50 eV photons were produced by the undulator beamline of Synchrotron Radiation Center at Madison, Wisconsin.

Experimental Procedure

The silica samples consisted of Type III and IV[5] high-purity synthetic silicas, specifically Suprasil W1 (dry), which contains about 5 ppm OH by weight, and Suprasil 1 (wet), which contains 1200 ppm OH. Total metallic impurities were of the order of 1 ppm.

Samples were cut from a 30 mm diameter and 1 mm thick disk to the dimensions 5 mm x 18 mm x 1 mm. The samples were cleaned, mounted on a sample holder attached to a manipulator, and inserted into an UHV (Ultra High Vacuum) chamber for the 50 eV irradiations. Several samples were mounted on the same holder. The same optical geometry for each sample was achieved by changing the height of the sample holder inside the UHV chamber. The experimental setup is shown in Fig. 1. The vacuum was kept at 10^{-9} torr during the 50 eV exposure at room temperature. For the 5 eV exposure, 50 mJ/cm^2 unfocused KrF excimer laser beam was used to expose the sample in air at room temperature. The total number of shots was 10^{10}.

The types and concentrations of paramagnetic defects produced by 5 and 50 eV light were measured by electron paramagnetic resonance spectroscopy (Brucker ESR 200 at 9.7 GHZ). The E' centers (singly charged oxygen vacancies) and oxygen-related centers were monitored at room temperature and 110K, respectively. The number of defects in silica was determined by comparison with a standard sample (a Brucker strong pitch secondary standard) whose paramagnetic state concentration was known. The error in the relative numbers of paramagnetic defects was ± 10%. The absolute numbers of paramagnetic centers has an error estimated at ± 100%.

The flux of 5 eV photons incident on a sample was determined through calculations based on measurements of power density and total number of pulses. The total number of 50 eV photons was also calculated from the exposure time and the photon flux. The photon flux was calculated from measurements of current produced in a calibrated gold diode and the photoelectric yield on gold.[6] The flux of 50 eV photon was $(1.1 \pm 0.1) \times 10^{18}$ photons per 1mm diameter spot per minute.

The irradiated volume was calculated from the 1/e penetration depth of 50 eV photons in silica and the beam diameter. The 1/e penetration depth was assumed to be 3.2 μm[7] and the beam diameter was 1 mm. Seven to fourteen spots were irradiated on each sample. We estimate the uncertainty of the diameter of the beam size as ± 30% when the distribution of photons across the beam is taken into account. The photon energy is lower than the bandgap energy in the case of the 5 eV photons; hence, the irradiation volume is the entire sample.

Results

Paramagnetic resonance spectra of E' centers and oxygen related (OR) centers, including peroxy radicals[8] and non-bridging oxygen hole centers[9] were detected in both 5 and 50 eV irradiated silicas. The concentrations of defects of each type in each sample were calculated from measurements of the number of defects and the irradiated volume. The defect formation rate per photon was obtained by dividing the total number of defects by the total number of photons.

The concentrations of defects, the defect formation per photon, the ratio of E' center to OR centers, and the total number of photons used in exposure are all listed in Table I and II.

The 50 eV light created about 10^{15} E' centers per cm^3 and about 10^{13} OR centers per cm^3 in both dry and wet silicas. The formation rate of E' and OR centers are 10^{-4} and 10^{-5} per photon respectively. The ratio of E' center to OR center is three times higher in wet silica than dry silica.

The 5 eV photons introduced about 10^{16} E' centers in both samples. These photons induced approximately 30 times higher concentration of OR centers in dry silica (6.0×10^{14}) than in wet silica (1.7×10^{13}). The formation rate of E' center is about 10^{-12} per photon in both silicas, and 6×10^{-13} and 1.6×10^{-15} OR center per photon in Suprasil W1 and Suprasil 1, respectively. The E'/OR Center ratio is 50 times higher in wet silica than dry silica and has the same trend as in 50 eV irradiated silicas.

Discussion

A flux of 10^{18} 50 eV photons create the same order of magnitude of E' and OR centers as 10^{26} 5 eV photons.[10] The absorption coefficient for the 5 eV photons in silica is about 7×10^{-3} cm^{-1},[10] while all the 50 eV light is absorbed. Taking this difference in absorptivity into account, the 50 eV light produces $\sim 10^5$ to 10^6 more defects than the 5 eV light.

Three possible reasons may explain this difference in defect formation per photon between the 5 and 50 eV photons. First, E' center formation by 5 eV photons may be due to a two photon process.[11] If this is the case, the low absorptivity for a two photon process, which is 2×10^{-3} cm^{-1},[12] would result in an absorptivity of $\sim 10^{-5}$ cm^{-1}. Thus, the ratio absorptivities for 5 eV and 50 eV photons is approximately 10^{-10}. The ratio of paramagnetic states produced by 5 eV to 50 eV photons is $\sim 10^{-12}$. Thus, the 50 eV photons produced ~100 times more paramagnetic defects than did the 5 eV photons. Second, Arai et al.[11] suggested that the E' center induced by 5 and 6.4 eV light is through hole capture at precursor sites. At a flux of 10^{21} 6.4 eV photons cm^{-2} the onset of saturation of E' centers was observed. This saturation effect may also occur for 10^{26} 5 eV photons cm^{-2}. In addition, the 50 eV photons may produce new E' and OR centers by Si--O bond breaking. The threshold energy for Si--O bond breaking is about 8.5 eV;[13] hence, in case of 50 eV photons we assume that their energy is sufficient to break Si--O bonds. Bond breaking process may well explain why 50 eV light produces 2 or 3 orders more defects in silica than 5 eV light.

Acknowledgement

This work was supported by the Naval Research Laboratory under contract number N00014-86-C2546 and partially supported by the University Research Initiative of the Air Force Office of Scientific Research under contract No. F49620-86-C0125DEF and in part by Office of Naval Research/SDIO contract No. N0014-87-C-0146. We thank the technical staff of the Synchrotron Radiation Center, University of Wisconsin, for the diligent application of their expertise on our behalf. The Synchrotron Radiation Center is supported in part by the National Science Foundation.

Table I Silicas Irradiated by 50 eV Light from Synchrotron

Silicas	E'(cm^{-3})	ORC(cm^{-3})	E'/Photon	ORC/Photon	E'/ORC	Total Photons
Sup W1	$1.1x10^{15}$	$6.4x10^{13}$	$3.0x10^{-4}$	$1.8x10^{-5}$	17	$3.7x10^{18}$
Sup 1	$3.3x10^{15}$	$6.7x10^{13}$	$4.5x10^{-4}$	$0.9x10^{-5}$	49	$7.4x10^{18}$
Error	(±40%)	(±40%)	(±50%)	(±50%)	(±20%)	(±10%)

$5.3x10^{17}$ photons per 5 mins per 1 mm dia. beam size

The penetration depth for 50 eV photon in silica is 3.2 μm

Table II 5 eV (248 nm) KrF Excimer Laser Irradiated Silicas

Silicas	E'(cm^{-3})	ORC(cm^{-3})	E'/Photon	ORC/Photon	E'/ORC	Total Photons
Sup W1	$6.8x10^{15}$	$6.0x10^{14}$	$6.0x10^{-13}$	$6.0x10^{-14}$	10	$7.8x10^{26}$
Sup 1	$8.5x10^{15}$	$1.7x10^{13}$	$8.0x10^{-13}$	$1.6x10^{-15}$	500	$7.8x10^{26}$
Error	(±40%)	(±40%)	(±50%)	(±50%)	(±20%)	(±10%)

50mJ per cm^2 per shot, total shots 10^{10}, total photons on .5 x .5 x .3 cm^3 = $7.8x10^{26}$

The absorption coefficient of 5 eV photon in silica is about 7.0 x 10^{-3} cm^{-1}

Oxygen Related Centers (ORC) include Peroxy Radicals (POR) and Non-Bridging Oxygen Hole Centers (NBOHC)

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